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9 Addendum to Final Report,
submitted to
Office of Naval Research
Contract No. N00014-75-C-0894 ✓
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6 COHERENT ANTI-STOKES RAMAN SPECTROSCOPY.
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G. L. Report No. 2751

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COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

Robert L. Byer and Mark A. Henesian

ABSTRACT

During the six months extension to the research program we have carried out two important measurements using the cw CARS technique. The first measurement gave an absolute Raman frequency of the Q(2) line of D₂ of 2,987.237₁ ± .001 cm⁻¹ which is two orders of magnitude more precise than previous values. In the second measurement effort we studied the pressure dependence and motional narrowing of the ν_1 band of methane.

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COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

I. SUMMARY OF RESEARCH PROGRAM

During this program, which was funded for one year and included a six month no cost extension, we carried out high resolution cw CARS research that led to five published papers and presentations at three international conferences.

The final report, submitted in March 1977, summarized our work to that time. Since then we have extended our research effort to the measurements discussed in Appendix I and Appendix II.

This addendum to the final report concludes our research under O.N.R. support. There is a considerable amount of spectroscopy yet to be done using the cw CARS method pioneered in our laboratory. We hopefully will be able to obtain support for future investigations.

APPENDIX I

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AN ABSOLUTE RAMAN FREQUENCY MEASUREMENT OF
THE Q(2) LINE IN D₂ USING CW CARS

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JUNE 1977

AN ABSOLUTE RAMAN FREQUENCY MEASUREMENT OF THE
Q(2) LINE IN D₂ USING CW CARS

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ABSTRACT

Coherent Anti-Stokes Raman Spectroscopy (CARS) is combined with high resolution interferometry to measure the absolute Raman shift of the Q(2) vibrational line in D₂⁺. The preliminary value found is $2,987.237_{\pm 1} \pm .001/\text{cm}^{-1}$. Such precision is essential for the testing of ab-initio energy level calculations for the hydrogen isotopes.

A study is also made of the pressure dependence of the nu(2) spectral band for methane (CH₄).

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AN ABSOLUTE RAMAN FREQUENCY MEASUREMENT OF THE Q(2) LINE IN D₂ USING CW CARS

It has long been recognized that forward Raman scattering in gases yields the narrowest lines^{1,2,3} and consequently permits the most precise determination of Raman frequencies. Qualitatively, for an isolated Raman transition, the line shape in coherent anti-Stokes Raman spectroscopy (CARS)^{4,5} is similar to the spontaneous Raman profile and can also be used for the same purpose. It is the object of this note to report such a measurement for the Q(2) component of D₂. A hydrogen isotopic molecule was chosen because a theoretical determination of the frequency may be made without involving the usual Born-Oppenheimer approximation.⁶ Thus such experiments are of fundamental importance in molecular spectroscopy.

Figure 1 shows a schematic layout of the apparatus. The argon pump laser produced 5 watts single frequency at 5145 Å while the dye laser produced about 50 mW single frequency near 6050 Å. Each laser was monitored with a filter (F₁, F₂) and spectral analyser (SA₁, SA₂) during the experiment. The two laser beams were combined using the constant deviation prism, P₁, and focussed into the cell with a 30 cm focal length lens, L₂. The three beams, Ar, dye and anti-Stokes, were collimated by L₃ and then dispersed by the second constant deviation prism P₂. Several points of interest about this arrangement warrant mention. The use of mirrors M₁, M₂ and the prism P₁ permitted a precise overlap of the two beams with little loss in intensity. The prism also dispersed the plasma lines from the argon laser so that they did not enter the cell. The use of diaphragms D₁, D₂, D₃, D₄, prism P₂, narrow band filter F₄ and the

spectrometer which was equipped with a holographic grating reduced the parasitic 5145 Å light at the CARS wavelength to a point below the dark count of the photomultiplier.

The signal from the 1 meter spectrometer only serves to indicate that the dye laser and argon laser are exactly separated in frequency by the Raman frequency. Having located the center of the CARS signal the Fabry-Perot interference rings were photographed first for the dye laser and then the argon laser. The spectral analyzer was used to ensure that the argon laser did not drift during the one minute time lapse between the two one second exposures. Filter F_3 reduced the intensities such that convenient equal time exposures could be taken while the moving ground glass screen S was used to provide ring patterns free of speckle effects. The ring diameters were measured on a traveling microscope and the fractional order ϵ determined in the standard way.

The principle of the experiment is straightforward. If d is the separation of the interferometer plates and N the integral order number then we have the equations $(N_A + \epsilon_A) = 2 d \nu_A$ and $(N_D + \epsilon_D) = 2 d \nu_D$ for the argon and dye laser lines respectively. Subtracting the two equations yields the final equation for the Raman frequency:

$$\nu_R = \nu_A - \nu_D = \{(N_A - N_D) + (\epsilon_A - \epsilon_D)\} / 2d = (N_O + \Delta\epsilon) / 2d$$

If d is known precisely then an approximate value of ν_R may be employed to determine the integral order number N_0 . This combined with our measured $\Delta\epsilon$ and d then yields a highly accurate value of ν_R . The interferometer spacing was measured first using a number of Hg lines^{7,8} and a Lamb dip locked helium-neon laser and then a final distance determined using an iodine locked helium-neon laser operating at the vacuum frequency of $15,798.0049 \text{ cm}^{-1}$.⁹ The interferometer was evacuated so that only vacuum frequencies were measured.

Figure 2 shows the CARS signal for the $Q(2)$ line of D_2 at six atmospheres at 24°C as a function of the dye laser frequency. The peak signal corresponds to about $4.5 \times 10^4 \text{ c/s}$. As the line appears symmetric one can safely assume that interference with the background electronic third order susceptibility is negligible and that the peak of the signal does indeed occur at the Raman frequency.¹⁰ The line was 650 MHz broad at 6 atm and showed the usual narrowing with reduced pressure.^{11,12,13,14} We estimate that the dye laser could be manually set at the line center within 50 MHz at the highest pressure and 30 MHz at the lowest pressure.

Figure 3 shows the measured difference in the fractional order, $\Delta\epsilon$, for the $Q(2)$ line of D_2 over a range of pressures. Of the twelve measured points the points marked a and b did not originally fall on a smooth curve but were off by an amount corresponding, within experimental error, with a mode jump of either one or two orders for the dye laser. Such erratic behavior of the dye laser was not uncommon. (The dye laser cavity has a F.S.R. of 390 MHz so that a jump of 1 order produces a $\Delta\epsilon$ of 0.130 for our 0.1 cm^{-1} Fabry-Perot interferometer).

The two points have been adjusted as indicated in Fig. 3 and lie close to the fitted line. A least squares curve fit excluding the adjusted four atmosphere points yields a straight line with a slope of -67.2 MHz/atm and a fractional order difference intercept of $\Delta\epsilon = .410 \pm .005$. The average root-mean-squared deviation of the line is computed to be $\pm 23.4 \text{ MHz}$ which is in excellent agreement with our estimate of the dye laser settability on the Raman line center. Theoretically the pressure shift should be of the same order as the Q(1) line for H_2 which is about -94 MHz/atm .¹⁵ Agreement for both the frequency shift and the mode hop frequency difference give us confidence that the intercept on the $\Delta\epsilon$ axis at zero pressure will yield the correct free molecule vacuum frequency.

With d equal to $4.9991697 \pm (1 \times 10^{-7}) \text{ cm}$ and using the approximate value of $2987.23 \pm .02 \text{ cm}^{-1}$ for ν_R ¹⁶ we find $N_0 + \Delta\epsilon$ to be $29,867.3(4) \pm .2$. Thus N_0 is 29,867. With our intercept for $\Delta\epsilon$ of $0.410 \pm .005$ we calculate ν_R to be $29,867.410/2 \times 4.9991697 = 2,987.237_1 \pm .001 \text{ cm}^{-1}$. This is the new value for the Q(2) line in D_2 and we have clearly demonstrated that CARS may be used for the ultra precise determination of Raman frequencies. The precision achieved is itself sufficient to critically test non-adiabatic corrections to the hydrogen isotope frequencies. With improvements particularly in the dye laser it should be possible to measure ν_R to $\pm .0001 \text{ cm}^{-1}$ or considerably more precise than all previous measurements.

One of us, namely A.D. May, (Toronto University), would like to thank Professor R.L. Byer for the extreme hospitality shown

during his brief visit to Stanford University. Appreciation on all our parts is also expressed to Spectra Physics, Professor A. Schawlow and Professor L. Stryer at Stanford University, and Dr. K. Billman at NASA/AMES Research Center, who generously loaned equipment and thereby made the experiment possible.

FIGURE CAPTIONS

1. Schematic layout of the apparatus for cw CARS in gases.
2. Profile of the Q(2) line in D_2 at 6 atm.
3. Difference in fractional order of interference for the Q(2) line in D_2 as a function of pressure.

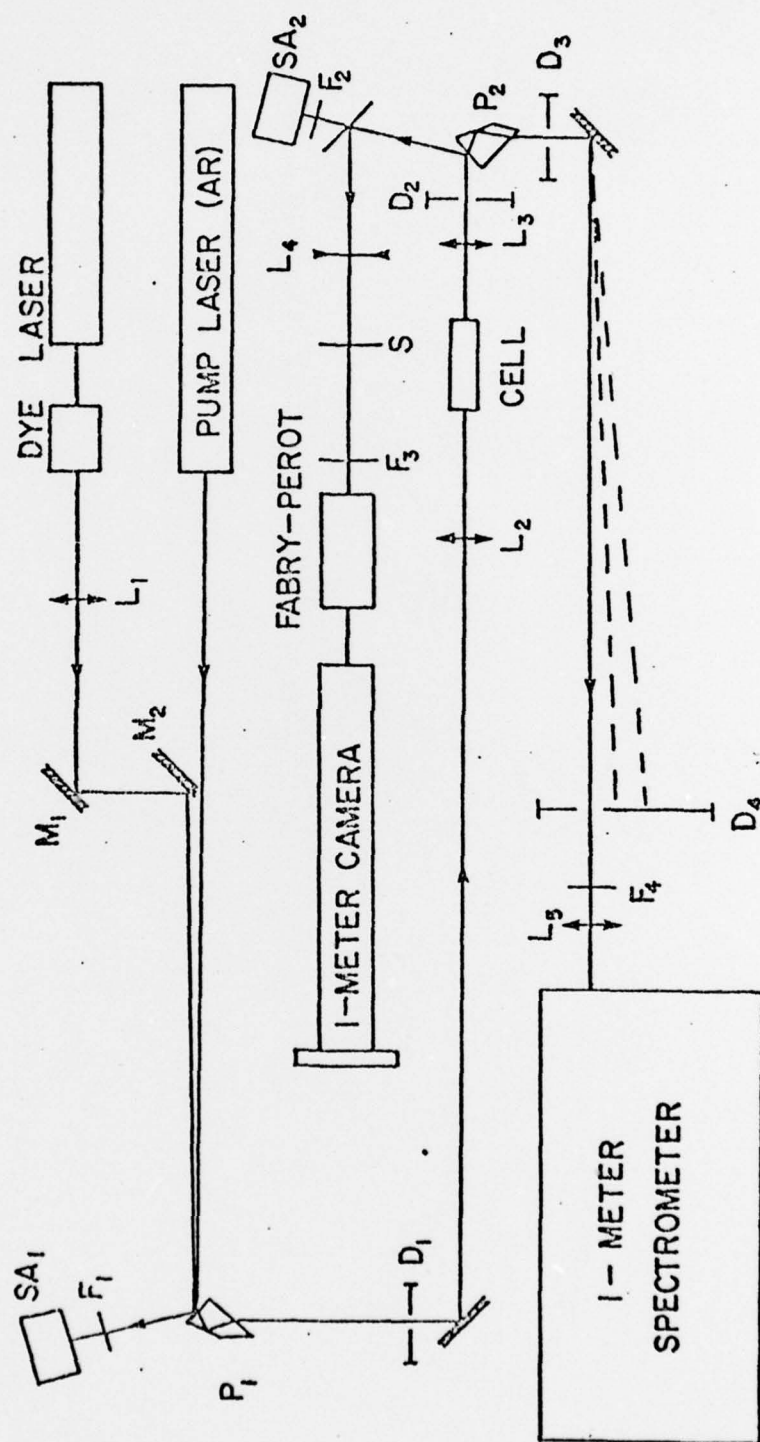


FIGURE 1

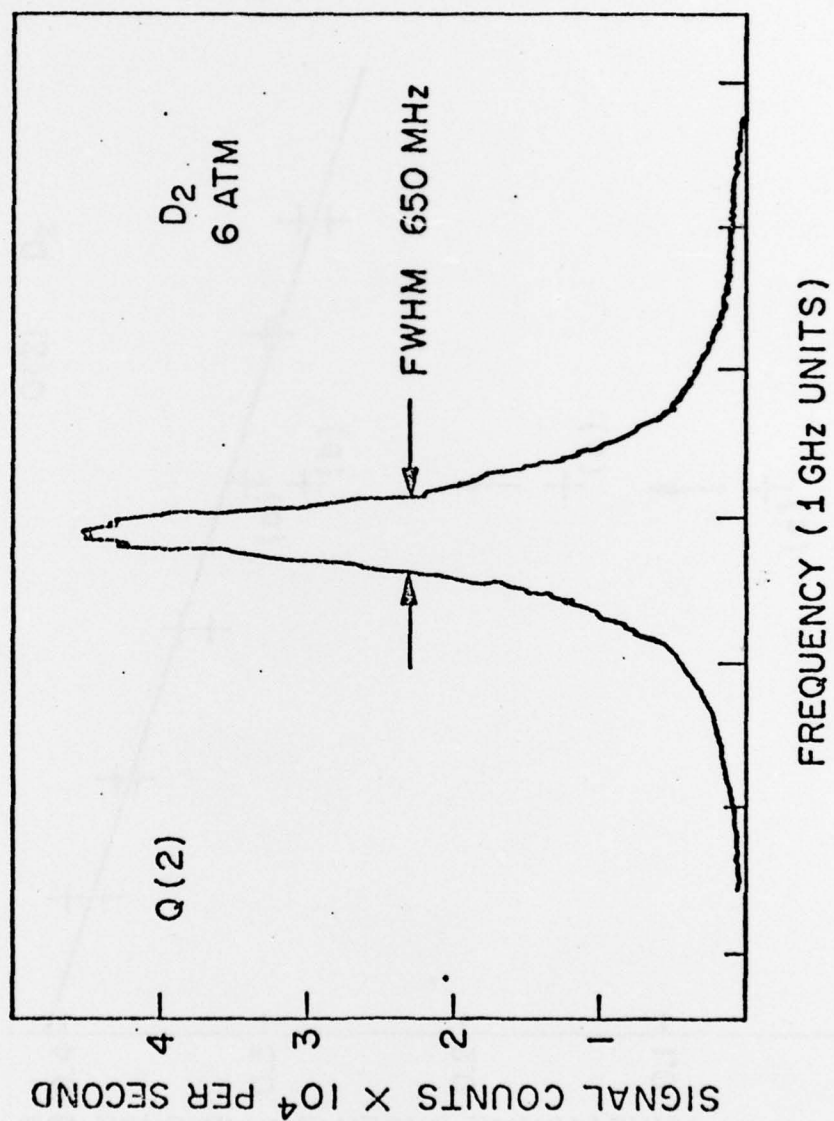


FIGURE 2

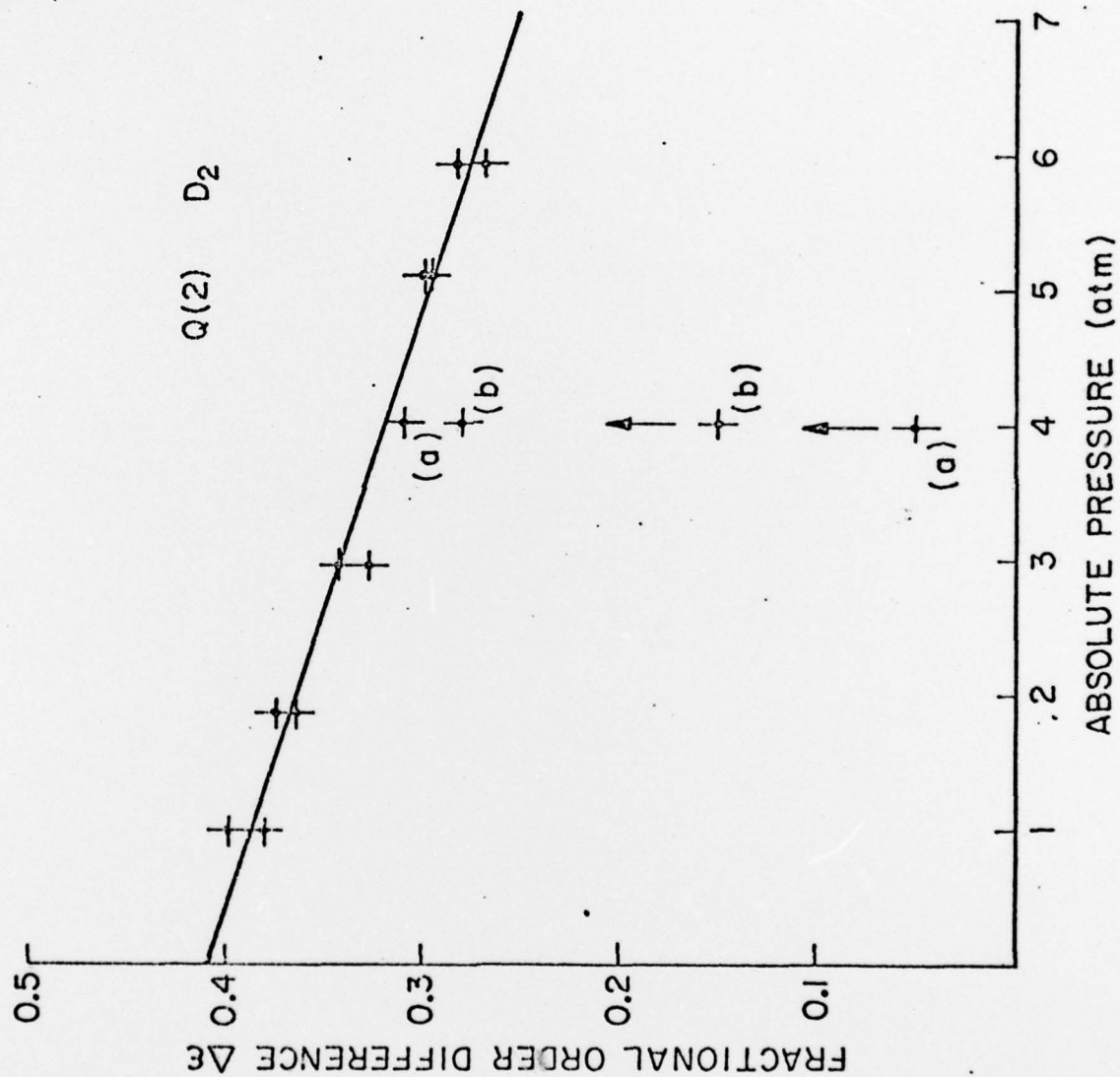


FIGURE 3

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APPENDIX II

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THE CW CARS SPECTRUM OF THE ν_1 BAND OF CH_4 AND ITS PRESSURE DEPENDENCE

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THE CW CARS SPECTRUM OF THE ν_1 BAND OF CH_4
AND ITS PRESSURE DEPENDENCE

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The ν_1 band of CH_4 has been studied in normal Raman spectroscopy at high resolution by Clements and Stoicheff¹ and by Boguillon et.al.,² using CARS. The spectra reported in the two papers are very different. Clements and Stoicheff observed at 2 atmospheres a partially resolved band degraded towards higher Raman frequencies and deduced as a result that B' was larger than B_0 with a difference, α_1 , equal to $-3.4 \times 10^{-3} \text{ cm}^{-1}$. Boguillon et.al., report a very complicated structure at 60 torr which bears no resemblance to the spectrum in reference 1 or to a normal Q branch. They did not attempt any analysis. It is the purpose of this note to report our preliminary observations for the ν_1 band of CH_4 as a function of density and to remove some of the misunderstandings concerning the true structure of the band.

The cw CARS spectrometer used was the same as that reported by Henesian et.al.,³ with the exception that the Fabry-Perot interferometer was not employed. Spectra in the region of the ν_1 band were recorded in two ways, one by continuously scanning the dye laser and the other, stepwise, by mode hopping the dye laser in steps of 390 MHz over a range of about 40 GHz. The frequency of the dye laser was monitored with a scanning interferometer with a spectral free range of 10 GHz. The Argon pump laser wavelength was also monitored and showed a very slow variation in frequency of $\pm 500 \text{ MHz}$

about its mean value. This variation while annoying does not affect the structure observed in the spectra. A number of runs were made at densities varying from 200 torr to 4.3 atmospheres, all at room temperature.

Figure 1 shows the results for a number of selected densities. The curves in 1A are for a single stepwise scan while 1B at higher dispersion is a composite made from three consecutive, continuous runs. At high density the band consists of a single smooth contour degraded towards higher Raman frequencies. As the density is lowered the band decomposes into three components. These results do not appear to be compatible with the results of either of the two papers referred to above. However, there are a number of gross features in common. At 2 atm. the band is broad with little structure and is degraded towards higher Raman frequencies. This is compatible with the observations of Clements and Stoicheff.¹ The CARS signal is narrower than the width of the spontaneous Raman spectrum as is to be expected. If one ignores the fine structure in the spectrum of Boguillon et.al.,² and compares their spectrum with that for 300 torr in Fig. 1 then the "peaks" at about 2917.1, 2916.8 and 2916.7 correspond exactly with the peaks at 11, 3 and -1 GHz respectively. At this level of detail all three experiments are in agreement.

There are a number of reasons to believe that the structure analyzed by Clements and Stoicheff is spurious. First, there is no known physical reason why B' should be larger than B_0 . Second, we have repeatedly scanned the spectrum both continuously and stepwise with a maximum resolution some 50 times greater than that of

Clements and Stoicheff and find no structure. Third, the observations in HD, N₂ and CO^{4,5} on motional narrowing[†] leads one to expect a continuous, structureless band. Thus we believe the structure reported in reference 1 is spurious.

The discrepancies between the present observations and those of Boguillon are, in our opinion, partly due to experimental difficulties. We noted during the continuous scans that whenever the dye laser operated in two modes there was a decrease of 25 to 30 percent in the CARS signal: the beat signal at 390 MHz was above the response of our detection system and the signal strength at this beat frequency was lost. The detection system (oscilloscope) of Boguillon et.al.,² probably has the same handicap. They also reported that their pulsed dye laser sometimes ran in two modes separated by 600 MHz. Thus it is likely that much of the fine structure shown in their Fig. 3 is due to the changing mode structure of their dye laser. This explains why their fine structure bears no resemblance to a normal Q branch, i.e. quadratically spaced lines with an intensity contour following the population of the rotational states (c.f. Herzberg).⁶ The apparent structure near the region 1 to 5 GHz in our Fig. 1B, is due to multi-moding of the dye laser. Such shortcomings of a CARS spectrometer must be overcome before reliable continuous spectra can be obtained and is the reason why in this note we have resorted to stepwise, but single mode scanning.

The question now arises as how to explain the present results. There are a number of observations which indicate that the strong central component seen at low densities is the Q branch of CH₄

and that the evolution of the spectrum with density is due to motional narrowing. At low densities the width of the central peak, which appears at 300 torr to extend beyond the weaker component centered near zero frequency, is some 3 to 6 times greater than the widths of the two weaker peaks. The central peak is asymmetric and degraded towards lower Raman frequencies while the others are symmetric. The frequency dependence of the strong component is different than that for the other two. The spectra shown in Fig. 1a were arranged one above the other by arbitrarily choosing the zero to coincide with the center of the profile at 4.3 atm. and then shifting the center of gravity of the band to follow the frequency measurements of May et.al.⁷ This analysis of the data indicates that the two weak components remain at the same frequency, whereas the strong component shifts rapidly to lower Raman frequencies with increasing density.

The central component is, therefore, of a different nature from the other two. The asymmetric, yet continuous profile at low densities and the continuous and nearly symmetric profile at high density is indicative of a normal Q branch undergoing motional narrowing (c.f. the Q branch of CO in reference 5). The band shape at the lower densities indicates that the normal Q branch is beginning to evolve. This is never a sudden process, the high J value lines can be expected to be free of motional narrowing effects before the closely spaced lines at low J. Thus we conjecture that the ν_1 band will break up into components

over a large range of density starting, say, at 500 torr and being totally resolved at, say, 5 torr.^{††}

There remains the problem of the two extra lines in our spectra and other lines in the spectrum of Buguillon et.al.² It is likely they belong either to the ν_3 or the $2\nu_2$ band and at high density are responsible for the spectrum being degraded towards higher Raman frequency. However, until CARS spectra of a quality comparable to the infrared work of Pine⁹ is available a positive identification will not be possible.

In summary, we have presented the cw CAR spectrum of CH_4 at a number of densities and tied together our observations with those of Clements and Stoicheff¹ and those of Buguillon et.al.² Furthermore, we have given a qualitative explanation of the spectrum along with some physical insight into its density behavior.

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[†]Although the theory of motional narrowing in CARS has not yet been worked out and promises to be extremely complex, it will probably be qualitatively similiar to that for spontaneous Raman scattering. Motional narrowing occurs when the inelastic collision frequency exceeds the frequency separation of the Q branch components.

^{††}Smirnov et.al.,⁸ have recently resolved, at 20 torr, the strong central component and unambiguously shown it to be the ν_1 band. This completely substantiates the arguments and the estimates given below.

